Materials Chemical Point of View for Durability Issues in Solid Oxide Fuel Cells

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ABSTRACT

Degradation in Solid Oxide Fuel Cell performance can be ascribed to the following fundamental processes from the materials chemical point of view: that is, diffusion in solids and reaction with gaseous impurities. For SOFC materials, diffusion in solids is usually slow in operation temperatures 800~1000°C. Even at 800°C, however, a few processes are rapid enough to lead to some degradations; namely, Sr diffusion in doped ceria, cation diffusion in cathode materials, diffusion related with metal corrosion, and sintering of nickel anodes. For gaseous impurities, chromium containing vapors are important to know how the chemical stability of cathode materials is related with degradation of performance. For LSM as the most stable cathode among the perovskite-type cathodes, electrochemical reduction reaction of CrO$_3$(g) at the electrochemically active sites is crucial, whereas the rest of the cathodes have the SrCrO$_4$ formation at the point where cathodes meet with the gases, leading to rather complicated processes to the degradations, depending on the amount and distribution of reacted Cr component. These features can be easily generalized to other impurities in air or to the reaction of nickel anodes with gaseous impurities in anode atmosphere.

Key words: SOFC, Degradation, Cr poisoning, Chemical potential diagrams, Ni-S interaction

1. Introduction

Degradation issues of solid oxide fuel cells are not new but closely related to the fabrication issues of solid oxide fuel cell stacks. Since materials selection, materials processing and stack design are closely related in developing SOFC stacks, degradation of stacks has been discussed only for those stacks which are successfully developed and operated. For example, the most successful SOFC stacks, namely, sealless tubular cells developed by Westinghouse Power Corp. exhibit excellent long term stability up to 70,000 h for cells and more than 30,000 h for systems with about 0.1% performance degradation per 1000 h. Despite this success in the sealless tubular cells, there have been growing interests in developing alternative SOFC stacks to overcome demerits of the sealless tubular cells, namely, low volume power density and high fabrication cost. Since many efforts have been focused on new generation materials (LSF, LSCF for cathode, LSGM for electrolyte, Ni/ScSZ or Ni/GDC for anode, ferritic alloys for interconnect), new cell design (anode support cell or metal support cell), and new applications (cogeneration systems for residential houses), degradation of such SOFC stacks exhibit complicated features due to differences in materials, design and operation temperature and condition associated with respective applications. In this review articles, we will focus on the more generalized features of degradation issues in terms of physicochemical driving forces for chemical changes, appropriate mechanisms for mass transfer associated with performance degradation and possible interaction of chemical changes and mechanical deterioration. Special focuses will be paid for the thermodynamic analysis on driving forces for diffusion and reactions and the SIMS analyses on interdiffusion across the interface and interactions with gaseous impurity; these achievements are main results of the NEDO SOFC projects.

2. Physicochemical properties associated with cell degradation

In our previous work, we utilize the two fundamental properties associated with the stability and reactivity of double oxides and complex oxides; namely the valence stability among possible various valences and the stabilization energy for formation double oxides from constituent oxides with selected valence. On the other hand, acidity/basicity is an important chemical idea for examining the stability and reactivity. It is therefore interesting to examine how the acidity/basicity appears in the enthalpy-based relations. Fig. 1 shows the enthalpy differences between oxysalts and oxides for respective metals particularly for hydroxides(a), carbonates(b) and chlorides systems(c). In Fig. 1(a), the vertical axis corresponds to the enthalpy difference given below.
\[ M_nO + H_2O = 2M_{n/2}(OH) \]  

\[ \Delta_{\text{ react}} G^\circ = 2\Delta f^\circ H^\circ (M_{n/2}(OH)) - \Delta f^\circ H^\circ (M_nO) - \Delta f^\circ H^\circ (H_2O) - T\{2\Delta f^\circ S^\circ (M_{n/2}(OH)) - \Delta f^\circ S^\circ (M_nO) - \Delta f^\circ S^\circ (H_2O)\} \]  

Since \( \Delta f^\circ H^\circ (H_2O) \) and the entropy term do not sensitively depend on the respective elements, the enthalpy difference between hydroxide and oxide, \( 2\Delta f^\circ H^\circ (M_{n/2}(OH)) - \Delta f^\circ H^\circ (M_nO) \), provides different behavior for various elements; data are taken from the thermodynamic database MALT for Windows\(^{12}\). Thus, this value can be regarded as a good measure for hydroxide formation reaction. Fig. 1(a) clearly indicates that alkali metal and alkaline earth metals exhibit anomalous behavior when this quantity is plotted against the formation enthalpy of metal oxides. Similarly, the enthalpy differences are plotted in Fig. 1(b) for carbonates and in Fig. 1(c) for chlorides. Compared with hydroxide, the carbonates show larger enthalpy differences for alkali and alkaline earth elements. For chlorides, enthalpy differences become further significant for basic oxides. These behavior in enthalpy difference comes from the difference in acidity among \( H_2O(g) \), \( CO_2(g) \), and \( Cl_2(g) \).

2.1. Acid-Base characteristics of cell components particularly for cathode materials

In Fig. 2, those components composing of respective cell materials are plotted in an arbitrary scale according to the acidity/basicity. For example, cathode materials are usually made of perovskite-type oxides consisting of the basic oxides such as \( La_2O_3 \) and \( SrO \) and the acidic oxide like Mn, Fe and Co oxides. On the other hand, YSZ electrolyte consists of weak basic oxide of \( Y_2O_3 \) and weak acidic oxide \( ZrO_2 \). At high temperature SOFCs, therefore, the reactivity of the \( La_2O_3 \) and \( SrO \) components in cathodes and the \( ZrO_2 \) component in electrolyte plate is the most important issue and from the stability point of view, \( La_2O_3 \) is selected because of their less reactivity with YSZ\(^{21}\). For intermediate temperature SOFCs, however, there arises another important features, in the acidity/basicity in the SOFC materials. Since the higher electrode activity is required for the IT SOFCs, active cathodes such as LSCF have to be adopted. This leads to a situation that the reaction of active cathodes with the YSZ electrolyte should be carefully avoided by utilizing a ceria-based interlayer. Even so, the less thermodynamic stability of LSF and LSC is not improved by this method so...
that the reactivity with other components should be examined in details as shown in what follows:

2.2. Acidity in terms of α(SrO) vs. α(La₂O₃) in cathodes

Cathode materials are made of those perovskite-type oxides consisting of La₂O₃, SrO, MOₓ(M = Mn, Fe, or Co). From the acidity/basicity relations, La₂O₃ and SrO are basic, while MOₓ(M = Mn, Fe, or Co) are acidic. Although the stabilization energy for those perovskite oxides is about the same, their reactivity/stability is different due to the difference in the valence stability of transition metal oxides with tetravalent or trivalent ions. As a result, the thermo-dynamic activities of La₂O₃ and SrO exhibit quite different values among those perovskite oxides. In Fig. 3, the chemical potential diagrams using log α(SrO) and log α(La₂O₃) as axes are presented for the La-Sr-M-O system at 1073 K and p(O₂) = 0.2 atm. The lowest values for log α(SrO) and log α(La₂O₃) are indicated by star marks for respective materials, (La₀.8Sr₀.2)MnO₃, (La₀.8Sr₀.2)FeO₃, and (La₀.8Sr₀.2)CoO₃. These marks clearly indicate that the thermodynamic stability is in the order of LSM > LSF > LSC.

2.3. Acidity/Basicity of gaseous impurities

In the high temperature SOFCs, the alkali metals are evaporated and exist as gaseous species such as NaOH(g). Similarly, acidic substances are also evaporated at high temperatures; the important gaseous compounds in SOFC environments are CrO₃(g), Cr₂O₃OH₂(g), Sr(OH)₂(g), SiO₂(g), CO₂(g), and SO₂(g).
Chemical interactions of such gaseous compounds and SOFC materials can be well interpreted in terms of the acidity/basicity. In Fig. 5, the magnitude of the chemical reactivity between the SrO component and the acidic substance is plotted using the logarithmic activity of SrO as a measure for acidity scale. From this scale, it is easily found how chemical reactions with impurities including gaseous impurities are different among LSM, LSF, and LSC.

2.4. Oxygen potential dependence of chemical interactions

In SOFC environments, materials are exposed under various oxygen potentials and temperatures. It becomes therefore essential to examine the equilibrium properties of...
P₂O₅(g, 10⁻⁶ atm) > B₂O₃
  > Cr₂O₃ (CrO₃, Cr₂O₃(OH)₃)
  > SiO₂ (Si(OH)₄)
SO₂(g, 10⁻⁶ atm) > MnO₂
  > ZrO₂
  > HBO₂(g, 10⁻⁶ atm) at P(H₂O)=10⁻² atm
  > Al₂O₃
  > Fe₂O₃
  > Cl₂(g)
  > CO₂(g, 1 atm)
  > CoO
  > HCl(g, 10⁻⁶ atm) at P(H₂O)=10⁻² atm

Fig. 5. Impurities and cells components scaled in term of the acidity derived from the logarithmic activity of SrO in the La-Sr-M-O systems shown in Fig. 4.

chemical reactions involved in the degradation of electrode materials. Since the SrO is focused in the previous section, the interaction of SrO with acidic gaseous substances is considered here. In Fig. 6, two types of the chemical potential diagrams are plotted for the Sr-M-O-H system (M = P, Si, B, Cr). One is the Ellingham diagrams for the M-O-H systems including gaseous species; as gaseous species, the partial pressure of 10⁻⁶ atm is adopted. Although the dominant species in the H-O subsystem is not explicitly shown, the borderline between the H₂O(g) dominant and the H₂(g) dominant regions is given in respective diagrams. Those diagrams indicate under what temperature and p(O₂) conditions those elements start to volatilize in what chemical form. For example, phosphor exists as various gaseous species throughout the considered region. Silicon has two gaseous species, namely, SiO₂(g) and Si(OH)₄(g). Appearing features are quite different for two species. Boron in SOFC environments exist essentially as gaseous species changing chemical form. Chromium has tendency of volatilization in oxidative atmosphere. Those acidic gaseous compounds react with SrO component to form the Sr-based double oxides as shown in type B chemical potential diagram which is constructed at 1073 K. Those double oxides are quite stable so that their stability region extends to the reducing atmosphere, indicating that in the anode atmosphere, those compounds can exist as solid materials. The Sr-B-O-H system indicates peculiar behavior that no double oxides are stable in the cathode atmosphere, but in the anode atmosphere, Sr₂B₂O₅ exist as stable solid oxide.

2.5. Chemical reactions of nickel anode with impurities

Nickel reacts with gaseous impurities in fuels. Recently, utilization of coal gasified gas has attracted attention so that the investigations on the effects gaseous impurities have been made in many laboratories particularly in US. Fig. 7 shows the typical Ellingham diagrams for impurities in fuels such as S, Se, As, and P. Those elements are typical impurities in coals, but S and P are frequently observed in a normal condition without coals.

Chemical reactions can be divided into two categories; namely, the intermetallic compound formation and the oxy-salt formation. Since impurities exist as gaseous species and reaction products are solid, the appearance region of these products starts from the low temperature side. For H₂S at 10⁻⁶ atm, no intermetallic compounds(nickel sulfides) are

![Fig. 6. Chemical potential diagram for the Sr-M-O-H systems (M = P, Si, B, Cr); type A is the Ellingham diagram plotted as ΔG(O₂) vs. T for the M-O-H systems, and type B is the generalized chemical potential diagrams at 1073 K plotted as ΔG(O₂) vs. (ΔG(Sr)-ΔG(M)) (M = P, Si, B, Cr).](image-url)
formed in the operating anode atmosphere. \( \text{H}_2\text{Se} \) has similar trends but the interaction with Ni is stronger than \( \text{H}_2\text{S} \). Even though both elements form no compounds in anode operating conditions. Some lowering in anode performance is well documented. As exhibits strong interaction in the intermetallic compounds so that nickel will be easily reacts...
with As-containing vapors to form the intermetallic compounds. For phosphor, the interactions for the intermetallic compound and the oxysalt formations are strong. Both can be formed under the anode operating conditions depending on oxygen potential and temperature. From those considerations, the following can be derived; i) For intermetallic binary compound formation, interaction is strong in the order of P>As>Se>S; ii) For oxysalt formation, the same order is expected.

### Table 1. Comparison in Cathode Materials for Their Stability, Reactivity Against Reactions with Zirconia, Chromium Vapor, The Main Factor Determining Chromium Poisoning is the Cathode Mechanism Determined by the Valence Stability

<table>
<thead>
<tr>
<th>items</th>
<th>LSM</th>
<th>LSF</th>
<th>LSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valence stability</td>
<td>Mn$^{4+}$ Stable</td>
<td>Re$^{3+}$</td>
<td>Co$^{3+}$/Co$^{4+}$</td>
</tr>
<tr>
<td>$O^{2-}$conductive</td>
<td>Nearly zero</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Cathode mechanism</td>
<td>Three phase boundaries</td>
<td>Two phase boundaries (Surface)</td>
<td></td>
</tr>
<tr>
<td>Reactivity with YSZ (A-site deficient)</td>
<td>Stable</td>
<td>SrZrO$_3$</td>
<td>La$<em>{2}$Zr$</em>{2}$O$_7$, SrZrO$_3$</td>
</tr>
<tr>
<td>Reactivity with Cr substitute</td>
<td>Cr$^{3+}$</td>
<td>SrCrO$_4$/SrCrO$_3$/Cr$^{3+}$/Cr$^{4+}$ substitute</td>
<td></td>
</tr>
<tr>
<td>Cr poisoning</td>
<td>significant</td>
<td>But causes various deterioration</td>
<td></td>
</tr>
</tbody>
</table>

### 3. Importance of electrode mechanism

Although the chemical reactivity is important in understanding the degradation phenomena, it is well recognized that the chemical reactivity alone cannot provide satisfactory explanation for degradation. To fully understand what is going on the electrode activity, it is essential to know the electrode reaction mechanism. In what follows, the thermodynamic properties which are strongly related with the electrochemical reactions are summarized to provide a basis of correlating the complicated degradation behavior with the physicochemical features.

### 3.1. Where are the electrochemical reactive sites are?

Electrochemical active sites are the place where the reactants meet with each other and charge transfer process takes places. For this purpose, mass transportation of reactants and products to and from those sites should be well maintained. Roughly speaking, there are two different electro-reaction mechanisms; one is based on the electrolyte-electrode-gas three phase boundaries and the other being the gas-electrode surfaces, in other words, two phase boundaries. This differences are compared with other properties in Table 1. In the former case, the electrochemical active sites should be located in a quite narrow region in the electrolyte plate-electrode interfaces. The LSM cathode and nickel anodes are of this type. In the latter case, the active site distribution should be determined from the magnitude of the ionic and the electron conductivity in mixed conductive electrodes and also the electrode activity. Usually, the electron conductivity is higher than the ionic conductivity in the electrode layer, leading to the distribution in the bottom area of the electrode layer. In this sense, the distribution of active sites is similar to that in the three phase boundary mechanism. Even so, the difference comes from the higher ionic conductivity of electrode materials, which makes the active site distribution wider than those at TPBs. This active site distribution determines the electrical potential distribution as well as the oxygen potential distribution. Furthermore, the cation chemical potential distribution in the vicinity of the active sites is also affected by the reaction site distribution.

The active site distribution is not unchanged but changes by many reasons. For example, the current density gives rise to some changes in the active site distribution and associated with current density distribution due to the non-linear behavior of the electrode activity in comparison with the linear behavior in the ionic or electron current flows. In the vicinity of the open circuit voltage, the electrode reaction resistance is bigger than the corresponding ohmic loss in the ionic or electronic paths. As a result, the active sites tend to distribute all over the electrode area. On the other hand, under the high current density, the electrode resistance is not so big compared with ohmic contribution so that current tends to be concentrated into a limited area of electrode active sites.

Similar redistribution of current density can be also taken place when a limited area of the electrode is damaged. This is one of factors which make it difficult to detect deterioration of materials as electrochemical performance change.

### 3.2. What happens on the electrochemical sites from the thermodynamic point of view?

Since the reactants and products should be transported to and from the sites, there should appear the chemical potential gradient for such species. The chemical reaction reaction takes place only at the sites so that enthalmic heats associated with the reversible reaction should be emitted at the sites, leading to heat evolution in this zone. Temperature distribution in the active site vicinity should depend on current density. When current density becomes doubled, heats evolved also become doubled. In addition to this reversible enthalpy part of the electrochemical reaction, heats are also evolved as a result of electrode resistance, in other words, overpotential. This therefore depends on the electrode activity. Bad electrodes tend to evolve more heats. Furthermore, the overpotential is also directly related to the oxygen potential gradient and related cation chemical potential gradient in the vicinity of active sites. Again bad electrode gives rise to larger oxygen potential gradient.

Thus, non-linear behavior of the electrode activity makes the situation complicated and deviated from expected linear behavior. There can be combined effects of current density, temperature, and overpotential etc.
4. Stability vs. Degradation issues in cathodes

In this section, actual cathode materials are considered in relation with degradation.

4.1. Stability of cathode/electrolyte interfaces

This issue first appeared in the early stage of the stack development just because the cathode/electrolyte interface is weak against the high temperature heat treatment. During this development, it has been clarified that the electrochemical performance is sensitively affected by the thermodynamic stability of the interface. This sensitivity is much larger than those expected from the normal detection limits of reaction products by SEM etc. This means that only a small amount of reaction products is enough to lead the performance degradation, when such products are located on the electrical path or electrochemical active sites. In view of the thermodynamic stability, there are no chances for LSF and LSC to have stable contacts with YSZ, whereas LSM can have the stable interface depending on the A-site nonstoichiometry.

4.2. Ceria-based interlayer

In the intermediate temperature SOFCs, active cathodes such as LSF, LSC or LSCF has to be utilized to achieve high performance at lower temperatures. This makes it inevitable to insert ceria-based layer between YSZ electrolyte and those active cathodes. This leads to greater improvements in long-term stability of the cathode/electrolyte interfaces. Even so, it should be pointed out that, strictly speaking, the interface of pervoskite cathodes and the rare-earth doped ceria is not stable enough. Since stabilization of the rare earth oxide dopant is not significant in ceria so that such rare earth oxide component tend to react with the transition metal oxide component in the pervoskite oxides. This leads to excess in the A-site cations in the pervoskite lattice, leading to a large driving force for the Sr component to diffuse through the ceria-based interlayer. On the other hand, it is hard to fabricate ceria-based interlayer into dense film. In addition, cerium ions exhibit faster diffusion across the ceria/zirconia interface, resulting in the Karkendall pore formation in the ceria side. As a result, surface diffusion or grain boundary diffusion becomes significant in such porous films. Thus, degradation of performance of the cathode/ceria/YSZ layer depends on the Sr migration and resulting SrZrO₄ formation in relation to the ionic path in the ceria/zirconia side.

4.3. Chromium Poisoning

Chemical properties of pervoskite cathodes with chromium containing species such as CrO₂(g) and CrO₃(OH)₂(g) is governed by the acid/base relation. The reactivity of LSM is quite small, whereas that of LSF or LSC is quite high. This is essentially the same as those reactions with zirconia. As shown in Table 1, this tendency is completely contrary to the observation on Cr-poisoning. In order to explain this discrepancy, we need to consider the differences in the electrode reaction mechanism as well as in the reactivity.

i) Essentially chromium containing gaseous species does not react with LSM and therefore can easily reach to the reaction active sites. On these sites, the electrochemical reduction of Cr⁴⁺containing species can occur. As a result, reaction product of Cr₂O₃ or Cr₃Mn₄O₁₀ is deposited on the sites, leading to the severe degradation. Note here that only a small amount of Cr is enough to lead degradation. Several %/1000h degradation of electrical potential under the constant current corresponds to the accumulation of several μm/cm² for active electrode area. Usually, this amount cannot be detected without using SIMS technique.

ii) For LSF, LSC, or LSCF, the SrCrO₄ formation is thermodynamically predicted and has been actually observed in various experiments. Even so, reactions of performance degradation with the formed SrCrO₄ are not simple depending on research groups, experimental condition, cell configuration etc. The crucial feature seems to be where and how much such SrCrO₄ are formed and accumulated. This is affected by the nucleation, the Sr diffusion in solid materials, or the Cr transportation in gases. When chromium containing vapors are well reacted with the SrO component in the cathode surface area, this acts as trap sites and blocked sites for Cr vapors to attack reaction active sites. In such a case, cathode performance is not degraded until accumulated SrCrO₄ leads to make damage on the gaseous permeability or electrical path. If, on contrary, reactivity of the SrO component in cathode layer is not well activated and as a result, those Cr containing vapors can reach to the active sites, cathode performance can be degraded. Again, it is expected that only a small amount of Cr is enough to damage one active site. Even so, in LSF, LSC, or LSCF, other sites can become active when some sites are damaged. This is because the high ionic conductivity inside cathode materials makes available many candidates active sites located throughout the cathode layer.

As summarized in Table 1, the loss stability of tetravalent ions, Co⁴⁺ and Fe⁴⁺, is crucial property which determines the mixed conductivity and the chemical reactivity simultaneously, leading to the differences in chromium poisoning among LSM, LSF and LSC. Complicated features in Cr poisoning of LSCF, LSF and LSCF are also originated from a variety of features with reaction product arrangement governed by nucleation and diffusion.

4.4. Impurities in air

Most popular impurities in air seem to be sulfur and silicon. Sulfur can be probably introduced into cells as metal sulfates and decomposed into metal oxides and sulfur oxides (SO₃ or SO₂). Silicon can be also introduced as silicates and reacted with water vapor to form Si(OH)₄ (see Fig. 6). As shown in Fig. 4, stability of LSM is about the same as SrSO₄ or SrSiO₃. For a long term operation, such impurities are necessary to be watched, while for LSF and LSC, reactivity is high so that careful examination is needed.
ments, the poisoning effects by sulfur oxides appear significantly in Sr doped SmCoO$_3$ and is rather small in LSM. This trend is the same as the reactivity of the Sr component in the perovskite cathodes. In this point, this poisoning effect is different from those by chromium vapors, suggesting that this difference comes from possible differences in formation mechanism among SrSO$_4$ and SrCrO$_4$ (nucleation, or associated diffusion properties).

4.5. La(Ni,Fe)O$_2$

This cathode is interesting in a sense that no Sr doping is adopted. Sr doping has been adopted to adjust the thermal expansion coefficient, electrical conductivity and cathode performance. However, this cathode provides a good example for Sr-less perovskite oxides. As discussed above, the SrCrO$_4$ formation is most important feature associated with chromium poisoning in IT SOFC cathodes. Since SrCrO$_4$ is not formed in this cathode, it seems reasonable to see that this cathode shows rather good stability against the chromium vapors. Even so, it should be pointed out that thermodynamic stability of LaNiO$_3$ is weak compared with LaMnO$_3$, LaFeO$_3$ and LaCoO$_3$. This implies that this cathode may suffer from other long-term stability issues such as lanthanum zirconate formation.

5. Stability vs. Degradation in anodes

Degradation of nickel cermet anode performance is caused by microstructure change (nickel sintering), carbon deposition, sulfur poisoning and other many factors. On the other hand, there are some diversity in understanding the electrode reaction mechanism. Although detailed mechanisms are not well established, the following can be described concerning the anode reaction mechanism in their relation to degradation.

1) Three phase boundaries (TPB). Basically, anode reactions proceed along the three phase (Ni, electrolyte or the oxide component in cermets, and gas).

2) Hydrogen is most electrochemically active fuels. For hydrocarbon fuels, therefore, hydrogen formation from CO or CH$_4$ with water vapor takes place in the TPB vicinity.

3) The electrolyte conductivity affects the anode performance. In a similar manner, the oxide component of nickel cermets affects anode performance in various ways. One of measures is the oxide ion conductivity; when YSZ, ScSZ and GDC are compared as the oxide component, GDC>ScSZ>YSZ is the sequence of the conductivity. For proton (water) solubility, YSZ and ScSZ are the same and GDC is two-order of magnitude higher. The electron conductivity is similar to the ionic conductivity; that is, YSZ and ScSZ are about the same and GDC has higher electron conductivity. Furthermore, sintering characteristics is important because this determines the microstructure of cermet anodes. This makes it difficult to directly compare the electrode performance among three cermet anodes. We made an attempt to compare in simplified patterned electrodes on flat oxide planes. SIMS analyses on such electrodes clearly clarified that mass transfer in the TPB vicinity is quite different between Ni/YSZ and Ni/doped ceria. Particularly, surface of nickel is well governed by the physicochemical properties, particularly by the proton solubility; in Ni/doped ceria system, nickel surface can be covered with oxygen which is transferred as water vapor from the TPB areas where protons in ceria react with oxide ions to emit water vapor.

4) Carbon deposition and sulfur poisoning have been investigated using various cermet anodes. There can be found one tendency that Ni/ScSZ is much better tolerance against carbon and sulfur than Ni/YSZ. In addition, Ni/ScSZ also shows some tolerance against carbon and sulfur. Most reasonable explanation will be given in terms of high oxide ion conductivity in ScSZ since the proton solubility and the electron conductivity are about the same.

5) Nickel sintering behavior exhibits quite interesting features. For example, when the high operation temperature is adopted in the first generation of SOFC stacks, nickel sintering takes place only after several thousand hour operation. In this sense, involved physicochemical property is slow bulk/surface diffusion. On the other hand, in the intermediate temperature operation, nickel sintering is expected to become minor phenomenon but has been observed in more frequent manners than in the high temperature SOFCs. Appearance period of time is in some cases quite short; furthermore, sintering features appear to be significant. These suggest that something may change in the physicochemical properties associated with sintering, although fundamental physics is unchanged. Most plausible property should be surface energy or surface diffusion changed by contamination, for example with sulfur. With decreasing temperature, sulfur adsorption becomes rapidly significant and also sulfur solubility in Ni gradually increases under the same oxygen chemical potential.

One important aspect of degradation of nickel anodes is thus strongly related with the mass transfer. Not only adsorbed species but also dissolved species will be important concerning surface energy and diffusion.

6. Failures from viewpoint of high temperature materials chemistry

Materials deterioration associated with changes in chemical composition, deformation, volume change, change in electrode activity etc can be realized as a result of mass transfers via gases or diffusion in solids or stresses caused by thermal cycles, redox cycles etc. Here, these physicochemical properties will be discussed in their relation to the SOFC operational conditions.

6.1. Gaseous species and their partial pressures

Mass transfer via gaseous phase is one of the most important features in materials science of SOFCs. Driving forces for gaseous mass transfer are 1) flows of air or fuels as car-

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rier gases and ii) partial pressure differences in respective species. The latter is determined mainly by temperature distribution, materials distribution for the cell components and the overpotential around the electrochemical active sites. Under the steady state condition, these features are unchanged so that the gaseous species are continuously conveyed during a long-term operation. As a result, an accumulated amount of the transferred substances becomes significant even when the partial pressure is quite small. Degradation of SOFC performance is closely related with such gaseous mass transfer in a quite low partial pressure.

One typical example is the chromium poisoning on LSM cathode. For an actual case, we evaluated the level of partial pressure of chromium vapors as shown in Fig. 8 and resulting accumulated amount of chromium oxides in the associated active sites; these are typically, $10^{-9} \sim 10^{-10}$ atm in air and 4 nm/cm² of active area after 100,000 h operation causing about 0.5~1.0%/1000 h voltage lowering. This indicates that if we will control the degradation rate less than 0.5%/1000 h, we have to have corresponding precise methods of controlling these materials behavior. For such direct attack phenomena, we should examine what kind of vapors can attack which electrodes. From experimental point of view, detection around the electrochemical active sites by SIMS will be quite useful, whereas the thermodynamic considerations will lead to specification which gaseous species can be reduced or oxidized on the active sites to cause degradation in a similar manner to chromium poisoning.

Another example of a small amount of transferred substances affecting deterioration is the formation of liquids inside the SOFC stacks. Since SOFCs consist all of solid materials, introduction of liquid substances inside stacks causes significant changes in kinetic features of reactions. Typical example is the hot corrosion of metal interconnects. Sodium and sulfur are popular contaminants so that there is a great chance for leading the formation of liquid substances consisting of Na₂SO₄-Na₂CrO₄-(NaCl) eutectics. In the intermediate temperature SOFCs, metal interconnects are used as important cell components. Such metal interconnects are anomalously corroded to form non-protective iron oxide scale. This is apparently caused by the presence of a small amount of liquid substances.

A similar anomalous reaction can be seen even on the ceramic materials. In Fig. 9, the reacted cathode layer is shown as those elemental maps for Cr and Sr which were detected by SIMS. Apparently a large particle of SrCrO₄ is formed inside (Sm,Sr)CoO₃ cathode layer facing the entrance area of air which conveyed some impurities such as Cr and S and maybe Na. In this region, apparently, the Sr diffusion inside cathode is enhanced. There is a great possibility of a small amount of liquid substances enhanced the diffusivities.

Another possible liquid formation is related to the interaction of Ni electrode with H₂S to form Ni-S eutectics. Appearance of such liquid substances strongly depends on partial pressure values of involved gaseous species, temperature and sometimes oxygen potential. In Fig. 10, the generalized Ellingham diagram is shown for the Ni-S-O-H system under the conditions of $p(H₂S)$ or $p(SO₂)=10^6$ atm as functions of temperature and oxygen potential. It clearly shows that even when the partial pressure of sulfur containing species is fixed, the appearance of liquid depends on temperature and oxygen potential. Under the SOFC operational condition, these areas is quite critical.

One of the important features of the high temperature materials chemistry is that the equilibria among multi-com-
ponent and multi-phase system are rather easily established among gases, liquids and solids. Usually, contaminants are conveyed from outside SOFC stacks; this means that new equilibria can be established along the flow of the contaminants. At first, contaminants in solids or gases will be decomposed to emit gaseous species as well as other decomposition products. Gaseous contaminants may react with the cell components to emit other gaseous species. A typical example is silica contaminants which can react with lanthanum chromite based ceramics to form lanthanum silicates and chromium oxide (or chromium containing vapors). This is one of the chromium sources inside SOFC stacks. Usually, lanthanum chromite will not emit the chromium containing species because the stabilization energy of LaCrO$_3$ is large enough to lower the equilibrium pressures. Reactions with silicon contaminants change the situation as described above.

### 6.2. Diffusion during operations

Solid reactions cannot proceed without diffusion inside solid materials. In this sense, diffusion properties determine...
the geometrical features of the reaction product arrangement, which is critically important in changes in the gaseous permeability of porous parts or in the electrical resistivity inside electrode materials. Diffusion properties of SOFC related materials are summarized in Fig. 11. As a guide for measuring the relation between mass transfer and diffusivity, we consider the following values: 10^6 s=30,000 h for operation time, 1 mm for diffusion length as a typical amount transferred. These conditions indicate that diffusion coefficient of 10^16 cm²/s becomes a critical value for considering the long-term stability of materials. From this criterion, diffusion in the CeO₂-base materials becomes more impact on mass transfer than ZrO₂ materials. Furthermore, grain boundary diffusion is significant in ceria-based oxides so that this becomes one of the key issues in the long term stability. For the perovskite materials, diffusivity is faster than in the fluorite-type materials. This is an important point when reactions of perovskite cathodes with gaseous species are considered. As shown in Fig. 9, the fast Sr diffusion in the (Sm,Sr)CoO₃ gave rise to a formation of large SrCrO₄ grain in the front of gaseous stream containing Cr vapors. This strongly suggests that the Sr diffusion is enhanced in this area compared with surrounding area where SrCrO₄ formation takes place homogeneously. Grain of SrCrO₄ showed the growth towards the direction where chromium vapors come. This implies that the presence of a small amount of liquid impurities enhances the Sr diffusion to be faster than the supplying rate of chromium vapors so that SrCrO₄ growth takes place the direction of gaseous upstream. Furthermore, SrCrO₄ grain is boll-tyke, indicating the fast diffusion inside/surface of SrCrO₄.

In many cases, the arrangement of reaction products inside the reaction zone is determined by the driving force as well as the reactive diffusion properties. Particularly, the three phase boundary (TPB) region is special in a sense that the oxygen potential and other related chemical potential may have a strong gradient due to the electrochemical overpotential appearing around the active sites. Furthermore, a small amount of mass transfer may result in a significant degradation of electrode performance. In this sense, mass transfer in electrolyte and electrodes are important in addition to the direct transportation via gaseous phase.

7. For Further Investigations

One of the characteristic features of the high temperature materials chemistry is that the equilibrium can be easily established among a multi-component and multi-phase system. This means that reaction speed is rather high so that only a small difference in energy can give rise to further mass transfer and chemical reactions. In particular, gaseous species play important role in establishing true equilibrium. In contrast, solid related equilibrium may have limitation in its establishment due to rather slow nucleation and diffusion. In view of this, liquid formation from gaseous species becomes crucial phenomena in examining a long term stability of solid oxide fuel cells. Furthermore, diffusion through grain boundaries is still important path for mass transfer. Although mass to be transported is rather small, effects can be significant when transported materials react with the main component to form harmful substances to the electrochemical cells. Since the materials behaviors described above are quite tiny, we need to have appropriate methods of investigating such behaviors of materials and plausible effects on electrochemical activities. We have shown that the SIMS technique is one of such good methods. Thermodynamic considerations on such tiny changes may lead to better understanding the long term stability.

REFERENCES


